

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Confirmation No. 7206

Yasuhiro TADA et al.

Attorney Docket No. 2006 0371A

Serial No. 10/574,111

: Group Art Unit 1797

Filed March 31, 2006

Examiner Ana M. Fortuna

VINYLIDENE FLUORIDE BASED RESIN POROUS HOLLOW YARN AND

METHOD FOR PRODUCTION THEREOF

Mail Stop: Amendment

SUBMISSION OF RULE 132 DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

THE COMMISSIONER IS AUTHORIZED TO CHARGE ANY DEFICIENCY IN THE FEE FOR THIS PAPER TO DEPOSIT ACCOUNT NO. 23-0975.

Sir:

On June 11, 2008 Applicants filed an Amendment in response to the Office Action of December 11, 2007.

In further support of the patentability of the presently claimed invention, Applicants are submitting herewith a Rule 132 Declaration which demonstrates the importance of stretching the layer of a vinylidene fluoride resin, and the use of a specific blend of types of polyvinylidene fluoride resins having an ultra-high molecular weight and a medium-to-high molecular weight in accordance with the present invention.

Respectfully submitted,

Yasuhiro TADA et al.

By:

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Group Art Unit: 1797

Yasuhiro TADA et al.

Examiner: Ana M. Fortuna

Application S.N.: 10/574,111

Filed: March 31, 2006

For: VINYLIDENE FLUORIDE BASED RESIN POROUS HOLLOW YARN AND METHOD FOR PRODUCTION

THEREOF

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

DECLARATION UNDER 37 CFR 1.132

- I, the undersigned, Yasuhiro TADA, hereby declare as follows:
- 1. I am a citizen of Japan and a resident of 18 · 13 Kamitamari, Omitama·shi, Ibaraki·ken 311·3436, Japan.
- 2. In March 1991, I received my Master of Engineering degree in polymer material science from the Faculty of Science and Engineering of Yamagata University.
- 3. Since April 1991, I have been employed at Kureha Corporation (formerly, Kureha Kagaku Kogyo Kabushiki Kaisha) and have conducted research and development in the filed of, among others, stretched polychlorotrifluoroethylene film and polyvinylidene fluoride hollow fiber membrane, in Polymer Processing & Products Research Laboratories of Kureha Corporation.

I am an inventor of U.S. Patent No. 5,833,070 regarding stretched polychlorotrifluoroethylene film and U.S. Patent No. 7,351,338 regarding polyvinylidene fluoride hollow fiber membrane.

4. I am one of the applicants of the application S.N.: 10/574,111

(hereinafter referred to as the instant application) and accordingly I am familiar with the specification and claims of the instant application.

- 5. Moreover, I have read carefully and I am familiar with the Official Action dated December 11, 2007, which action rejected Claims 1-8 of the instant application. I have read carefully and I am familiar with several references, inclusive of Takamura et al (US 6, 299,773), Nohmi et al (US 4,399,035) and Morikawa et al (US 7,258,914) which are hereinafter referred to as Takamura ('773), Nohmi ('035) and Morikawa('914), respectively. The substance of the Examiner's rejection from the prior art aspect is believed to be based on the conclusion that Claims 1-7 are anticipated by or, in the alternative obvious over Takamura ('773); claims 1-3 and 6 are obvious over Nohmi ('035) or Morikawa('914).
- 6. In view of the Examiner's rejection, the applicants have amended claim 1 of the instant application based on the features of claims 5 and 8 as filed of the instant application to recite: that the claimed porous hollow fiber comprises a stretched single layer of a vinylidene fluoride resin; and that the vinylidene fluoride resin comprises 2-49 wt.% of a first vinylidene fluoride resin having a weight-average molecular weight (Mw1) of 4×10^5 - 12×10^5 and 51-98 wt.% of a second vinylidene fluoride resin having a weight-average molecular weight (Mw2) of 1.5×10^5 - 6×10^5 provided that the weight-average molecular weight (Mw1) of the first vinylidene fluoride resin and the weight-average molecular weight (Mw2) of the second vinylidene fluoride resin satisfy a ratio Mw1/Mw2 of at least 1.2.
- 7. For demonstrating the importance of the stretching and the use of a specific blend of two types of polyvinylidene fluoride (PVDF) having an ultra-high molecular weight and a medium-to-high molecular weight not disclosed by any of Takamura ('773), Nohmi ('035) and Morikawa('914), I made, under my direction and control some experimental tests, the procedure and the results of which are reported hereinbelow.

<EXPERIMENTS>

(Comparative Example A)

The production of a hollow fiber membrane was tried by using a single species of polyvinylidene fluoride (PVDF) having a weight-average molecular

weight of 4.90 x 10⁵ instead of the PVDF used in Example 7 otherwise in a similar manner as in Example 7 of the instant application. In the comparative test, however, a nozzle having a nozzle having an annular slit of 6 mm in outer diameter and 4 mm in inner diameter was used instead of the nozzle having an annular slit of 5 mm in outer diameter and 3.5 mm in inner diameter because of unavailability of the latter nozzle due to optimization of the nozzle after the instant application.

More specifically, a first intermediate form (i.e., a hollow fiber before extraction of the plasticizer) was prepared in the same manner as in Example 7 of the instant application except that the nozzle having an annular slit of 6 mm in outer diameter and 4 mm in inner diameter was used, and correspondingly, air was injected into a hollow part of the extruded fiber at a rate of 4.7 ml/min. and the extruded and cooled fiber was taken up at a rate of 3m/min., wherein the latter two modifications were adopted so as to provide a first intermediate form having an outer diameter of 1.943 mm and an inner diameter of 1.374 comparable to those if the first intermediate form of Example 7.

The first intermediate form was then subjected to extraction with dichloromethane, drying to remove the dichloromethane and heat treatment in the same manner as in Example 7 to prepare a second intermediate form (i.e., an unstretched hollow fiber membrane).

The second intermediate form was longitudinally stretched at a ratio of 1.35 times (substantially lower than 1.7 times in Example 7) at an environmental temperature of 25 °C, whereas the fiber was severed. Accordingly, the longitudinal stretch ratio was lowered to 1.30 times to obtain a stretched hollow fiber membrane, which was then subjected to two times of immersion in dichloromethane and heat fixation in the same manner as in Example 7 to obtain a stretched porous hollow fiber membrane.

The properties of the unstretched and stretched hollow fiber membranes were evaluated in the same manner as described in the instant application. The outline of the production conditions and the measured properties were show in the attached Table $\bf A$

In Table A, the outline of the production conditions and the measured properties of the stretched hollow fiber membrane of Example 7 shown in Table 1 of the instant application and the stocked data of the corresponding unstretched hollow fiber membrane, are also included for convenience of comparison.

<EVALUATION>

In view of the results shown in Table A, the following evaluation is believed to be readily derivable.

- (1) From a comparison between Example 7 and Example 7(Unstretched), a remarkable increase in basic water permeability as an essential performance of a hollow fiber membrane for water treatment is attained can be attained as a result of stretching.
- (2) From a comparison between Example 7 and Comparative Example A, the use of a specific blend of two types of polyvinylidene fluoride (PVDF) having an ultra-high molecular weight and a medium-to-high molecular weight remarkably facilitate the stretching of a yet-unstretched hollow fiber membranes.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: July 4, 2008

Yasuhiro TADA

Attachment: Table A

Table A:

Starting	82.5 8 82.5 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	9.36 4.12 2.27 5/95 4.38 - - - - - - - - - - - - -	4.90 4.90 	Unstretched (x1.35 stretch (x1.30 stretch d) 2.36 4.12 4.12 4.12 4.90 4.90 4.90 4.90 4.90 4.90 4.90 4.90 4.90 4.90 4.90 4.90 4.90 4.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.90 6.9	(Unstretched)
Ist. PVDF's Mw (Mw1) (x 10 ⁵) 2nd. PVDF's Mw (Mw2) (x 10 ⁵) Mw1/Mw2 Mw1/Mw2 Mw1/Mw2 Mw1/Mw2 Mw1/Mw2 Mw1/Mw2 Mixture's Mw (x 10 ⁵) Mw/Mn Polyester plasticizer Solvent Mixture B Plasticizer/solvent Mixture A/Mixture B Plasticizer/solvent Mixture B Plasticizer/solvent Mixture B Plasticizer/solvent Mixture B Mixture B		9.36 4.12 2.27 5/95 4.38	4.90		
Ist. PVDF's Mw (Mw1) (x 10²) 2nd. PVDF's Mw (Mw2) (x 10²) Mw1/Mw2 Mw		4.12 2.27 5/95 4.38 - - - - - - - - - - - - - - - - - - -	4.90 - - - - - - - - - - - - - - - - - - -	4.90 - - - - - - - - - - - - - - - - - - -	4.90 - - - - - - - - - - - - - - - - - - -
Supply rate (ml/min) Nozzle I. D. (mm)		4.12 2.27 5/95 4.38 - - - - - - - - - - - - - - - - - - -	4.90 - - - - - - - - - - - - - - - - - - -	4.90 - - - - - - - - - - - - - - - - - - -	4.90 - - - - - - - - NMP 82.5/17.5 35.7/64.3
Mixture A Ist. PVDF/2nd. PVDF mixing ratio (wt. %) Mixture's Mw (x 10 ⁵) Mixture B Mixture B Supply ratio (wt. %) Plasticizer/solvent Mixture A/Mixture B Solvent Supply ratio (wt. %) Mixture B Nozzle J. D. (mm) Mixture (ml/min) Air supply ratio (wt. %) Mixture (ml/min) Air supply ratio (mm) Mater bath temp. (ℂ) Air supply rate (ml/min) Mixture (ml/min) Obefore extraction (mm) Di before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Inner diameter Di (mm) Thickness (mm) Thickness (mm) Porosity (%) Ave. pore size P (μm)		5/95 5/95 4.38 4.38 - - - - - - - - - NMP 82.5/17.5 35.7/64.3 5 3.5 6.2	- - - - - - - - - NMP 82.5/17.5	- - - - - - - - - NMP 82.5/17.5 35.7/64.3	- - - - - - NMP 82.5/17.5 35.7/64.3
Mixture A 1st. PVDF/2nd. PVDF mixing ratio (wt. %) Mixture's Mw (x 10 ⁵) Mixture B Sulvent Solvent Supply ratio (wt. %) Mixing ratio (wt. %) Mozzle O. D. (mm) Mixing ratio (wt. %) Air supply rate (ml/min) Air supply rate (ml/min) Air supply rate (ml/min) Air supply rate (ml/min) Do before extraction (mm) Di before extraction (mm) Di before extraction (mm) Di before extraction (mm) Outer diameter Do (mm) Stretch ratio (times) Inner diameter Di (mm) Porosity (%) Ave. pore size P (μm)		5/95 4.38	- - - - - NMP 82.5/17.5	- - - - - - - - NMP 82.5/17.5 35.7/64.3	- - - - - - NMP 82.5/17.5 35.7/64.3
Mixture's Mw (x 10 ⁵) Mixture's Mw (x 10 ⁵) Mixture Solvent Mixture A/Mixture B Supply ratio (wt. %) Mixture A/Mixture B Supply ratio (wt. %) Nozzle O. D. (mm) Air supply rate (ml/min) Air supply rate (ml/min) Obefore extraction (mm) Di before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Inner diameter Di (mm) Porosity (%) Ave. pore size P (μm)		4.38 - - - - - - - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -	- PN-150 NMP 82.5/17.5 35.7/64.3
Mixture's Mw (x 10°) Mw/Mn Mw/Mn Polyester plasticizer Solvent Solvent Mixture B Supply ratio (wt. %) Mixture B Supply ratio (wt. %) Mixture B Supply ratio (wt. %) Mixture B Nozzle O. D. (mm) Air supply rate (ml/min) Air supply rate (ml/min) Water bath temp. (C) Take-up speed (m/min) Do before extraction (mm) Do before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Outer diameter Do (mm) Inner diameter Di (mm) Thickness (mm) Porosity (%) Ave. pore size P (μm)	4.38 - - - - - - - - - - - - - - - - - - -	4.38 - - - - - - - NMP 82.5/17.5 35.7/64.3 5 3.5 6.2	- - - - - - - - - - - - - - - - - - -	PN-150 NMP 82.5/17.5 35.7/64.3 6	PN-150 NMP 82.5/17.5 35.7/64.3
Mixture B Polyester plasticizer Mixture B Solvent Solvent Mixture A/Mixture B Supply ratio (wt. %) mixing ratio (wt. %) Nozzle O. D. (mm) Mozzle I. D. (mm) Air supply rate (ml/min) Air supply rate (ml/min) Air supply rate (ml/min) Do before extraction (mm) Do before extraction (mm) Di before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Thickness (mm) Inner diameter Di (mm) Thickness (mm) Porosity (%) Ave. pore size P (μm)	- PN-150 NMP 82.5/17.5 35.7/64.3 5 5 3.5 6.2	PN-150 NMP 82.5/17.5 35.7/64.3 5 5 3.5 6.2	- PN-150 NMP 82.5/17.5 35.7/64.3	PN-150 NMP 82.5/17.5 35.7/64.3	PN-150 NMP 82.5/17.5 35.7/64.3
Mixture B Plasticizer Solvent Mixture A/Mixture B Solvent Supply ratio (wt. %) mixing ratio (wt. %) Nozzle O. D. (mm) mixing ratio (wt. %) Nozzle I. D. (mm) Air supply rate (ml/min) Air supply rate (ml/min) Air gap (mm) Water bath temp. (C) Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Di before extraction (mm) Cuter diameter Do (mm) Thickness (mm) Thickness (mm) Porosity (%) Ave. pore size P (μm)	PN-150 NMP 82.5/17.5 35.7/64.3 5 5 3.5 6.2	PN-150 NMP 82.5/17.5 35.7/64.3 5 5 3.5 6.2	NMP 82.5/17.5 35.7/64.3	PN-150 NMP 82.5/17.5 35.7/64.3	PN-150 NMP 82.5/17.5 35.7/64.3
Mixture B Solvent Mixture A/Mixture B Plasticizer/solvent Supply ratio (wt. %) mixing ratio (wt. %) Nozzle O. D. (mm) Mozzle I. D. (mm) Air supply rate (ml/min) Air gap (mm) Air gap (mm) Water bath temp. (°C) Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Thickness (mm) Thickness (mm) Porosity (%) Ave. pore size P (μm) Ave. pore size P (μm)	82.5/17.5 35.7/64.3 5 3.5 6.2	NMP 82.5/17.5 35.7/64.3 5 3.5 6.2	NMP 82.5/17.5 35.7/64.3	NMP 82.5/17.5 35.7/64.3 6	NMP 82.5/17.5 35.7/64.3
Mixture A/ Mixture B Plasticizer/solvent Supply ratio (wt. %) Mixture B Supply ratio (wt. %) Nozzle O. D. (mm) Nozzle O. D. (mm) Air supply rate (ml/min) Air supply rate (ml/min) Air supply rate (ml/min) Air supply rate (ml/min) Do before extraction (mm) Do before extraction (mm) Di before extraction (mm) Di before extraction (mm) Air supply Outer diameter Do (mm) Thickness (mm) Porosity (%) Ave. pore size P (μm)	82.5/17.5 35.7/64.3 5 3.5 6.2	35.7/64.3 5 3.5 6.2 6.2	82.5/17.5	82.5/17.5 35.7/64.3 6	82.5/17.5 35.7/64.3
Mixture A/ Mixture B Supply ratio (wt. %) Nozzle O. D. (mm) Nozzle I. D. (mm) Air supply rate (ml/min) Air supply rate (ml/min) Air gap (mm) Water bath temp. (C) Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Di before extraction (mm) Take-up speed (m/min) Air supply rate (mlmin) Take-up speed (m/min) Take-up speed (m/min) Are-up speed (m/min) Are-up speed (mm) Thickness (mm) Porosity (%) Ave. pore size P (μm)	35.7/64.3 5 3.5 6.2	35.7/64.3 5 3.5 6.2	35.7/64.3	35.7/64.3	35.7/64.3
Nozzle O. D. (mm) Nozzle O. D. (mm) Air supply rate (ml/min) Air supply rate (ml/min) Air gap (mm) Water bath temp. (C) Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Inner diameter Do (mm) Thickness (mm) Porosity (%) Ave. pore size P (μ m)	3.5	3.5		9	.
Nozzle I. D. (mm) Air supply rate (ml/min) Air gap (mm) Water bath temp. (C) Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Di before extraction (mm) Tretch ratio (times) Outer diameter Do (mm) Inner diameter Di (mm) Thickness (mm) Porosity (%) Ave. pore size P (μ m)	3.5	3.5	9	֓֡֓֜֝֓֜֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֡֓֓֓֓֓֓֡֓֓֡֓֡֓֡֓	v
Air supply rate (ml/min) Air gap (mm) Water bath temp. (C) Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Inner diameter Di (mm) Thickness (mm) Porosity (%) Ave. pore size P (μ m)	6.2	6.2	4	4	4
Air gap (mm) Water bath temp. (C) Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Inner diameter Di (mm) Thickness (mm) Porosity (%) Ave. pore size P (μ m)		07.1	4.7	4.7	4.7
Water bath temp. (°C) Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Inner diameter Di (mm) Thickness (mm) Porosity (%) Ave. pore size P (\mu m)	170	170	170	170	170
Take-up speed (m/min) Do before extraction (mm) Di before extraction (mm) Stretch ratio (times) Outer diameter Do (mm) Inner diameter Di (mm) Thickness (mm) Porosity (%) Ave. pore size P (\mu m)	09	9	09	09	09
n) (t	5	2	3	3	3
(1)	1.949	1.949	1.943	1.943	1.943
	1.378	1.378	1.374	1.374	1.374
	1.7	1.00	1.35	1.30	1.00
Di (mm) (μ m)	1.57	1.697	* 3	1.453	1.580
(π m)	1.072	1.173		1.052	1.147
	0.249	0.262		0.200	0.217
	75.9	63.3		57.9	54.1
	0.131	0.070		0.095	0.055
	0.277	0.153		0.190	0.150
C value (/day, 100kPa at 25°C)	Ц	-0.001		-0.01	-0.002
water permeaning Fo value $(m^3/m^2 \cdot day, 100 \text{kPa} \text{ at } 25 \text{ C})$	a at 25°C) 72.2	11.8		50.1	4.8
	551.1	169.5		529.1	87.3
Fo/Di ⁴ 54.	54.7	6.2		41.0	2.8
Tensile strength (MPa)	10.9	10.2		10.1	5.8
Elongation at break (%)	18.2	141		6.6	51.2